

# Evolution of Quantum Theory



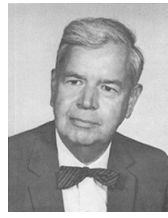
E. Schrödinger



P. A. M. Dirac



D. R. Hartree



J. C. Slater



P. Hohenberg



W. Kohn



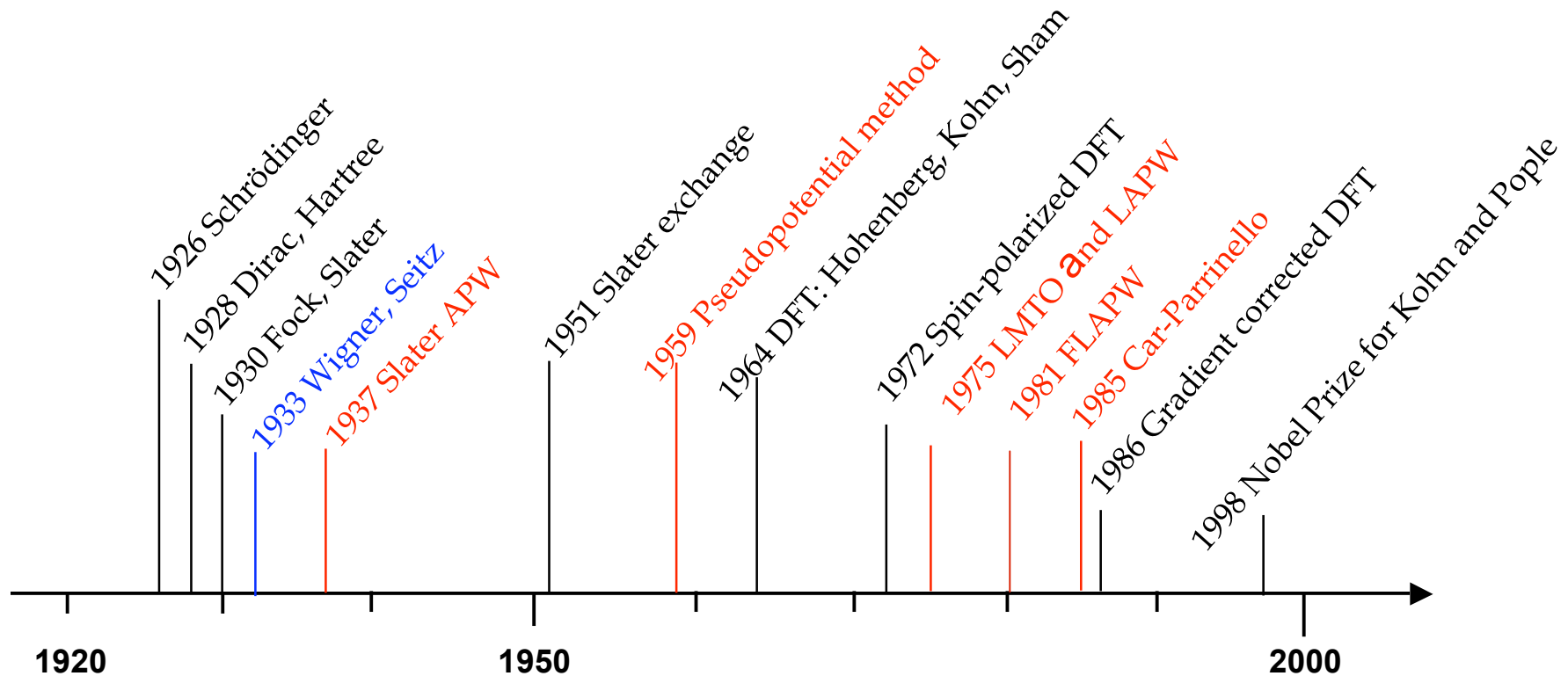
L.J. Sham



J. Pople



A. J. Freeman



# Computational Physics Today

- A means to understand **complex phenomena** that goes beyond the limitations of analytic theory
- **The Third Branch of Physics** – along with Analytic Theory and Experiment.
- Modeling/simulation as “**experimental theory**” or “**theoretical experiments**”.
- Relies on understanding the limitations and idiosyncrasies of the equipment – the **Computer**.
- Still in its infancy – 40 years vs. > 400 years of experimental physics.
- Of rapidly growing importance and impact for basic research and device applications.

**HOW DID WE GET HERE?**

# Road to Density Functional Theory

- **Schrödinger-Dirac Equation: “God’s Law”**

$$\sum_{\beta} \left[ \sum_{\mu} (\gamma_{\mu})_{\alpha\beta} \frac{\partial}{\partial x^{\mu}} + \frac{mc}{\hbar} \delta_{\alpha\beta} \right] \psi_{\beta} = 0,$$
$$x^{\mu} = \vec{x}, ict$$

Dirac was so impressed with the beauty of the theory that he said *“The advent of quantum mechanics has turned Chemistry into a branch of Applied Mathematics”* (1926)

For him the problem was fully solved – for the rest of us it took 80 years so far, and still counting.

- **Hartree-Fock Theory** satisfies Pauli principle with a many-electron wave function. Wavefunction is a determinant of single particle wavefunctions. Complex set of coupled integral differential equations. Treats exchange between pairs of same spin electrons exactly. Successful for atoms and molecules. ( Hartree and Hartree )

# Road to Density Functional Theory

- For solids, there was the seemingly simple **band equation**:

$$\{K.E. + V(r)\} \psi_k(r) = \varepsilon_k \psi_k(r)$$

$V(r)$  = periodic potential

**But what is  $V(r)$ ?**

This has been the **struggle** since the **early 1930's**  
**(Wigner, Seitz, Slater) – now conquered by DFT**

# Road to Density Functional Theory

- Important simplification of Hartree-Fock theory by Slater (1951)

$$V_{ex}(r) = \alpha \rho^{1/3}(r)$$

where  $\rho(r)$  is the charge density **locally** at point  $r$ .

The result is the simple band theory potential energy

$$V(r) = V_{coul}(r) + \alpha \rho^{1/3}(r) = \textit{periodic}$$

Surprisingly, this led to some important applications for magnetism.

# Impact of Early Energy Band Studies in Magnetism

- Band theory accounts for the non-integral atomic magnetic moments in Fe, Co, and Ni metals and transition metal alloys.
- An early remarkable success:
  - John Wood (1962) calculated the bands of paramagnetic bcc Fe;
  - Mick Lomer (1962) used a rigid band model to determine the bands of Cr
    - predicted the Fermi surface nesting (“balls and jacks”) and obtained the famous SDW.
- **4f Rare-earth metals** – Dimmock, Freeman and Watson (1964)
  - Completely transformed previous understanding of **anomalous** electronic, optical and magnetic properties of rare-earths as that of free-electron metals.
  - Demonstrated that they are like transition metals (5*d* and 6*s*, *p* conduction bands) but with localized 4*f* electrons.

# Basic Concepts of Density Functional Theory

## Hohenberg-Kohn Theorem (1964)

$E_{tot} = E[\rho]$  and is a minimum for the  
ground state density

## Kohn-Sham Equations (1965)

$$[K.E. + V_{eff}(\rho)]\psi_i = \varepsilon_i \psi_i$$

$$V_{eff}(\rho) = V_{coul}(\rho) + \mu_{xc}[\rho]$$

$$\rho = \sum_i |\psi_i|^2$$

$\mu_{xc}$  is the exchange **and** correlation potential

# Basic Concepts of Density Functional Theory

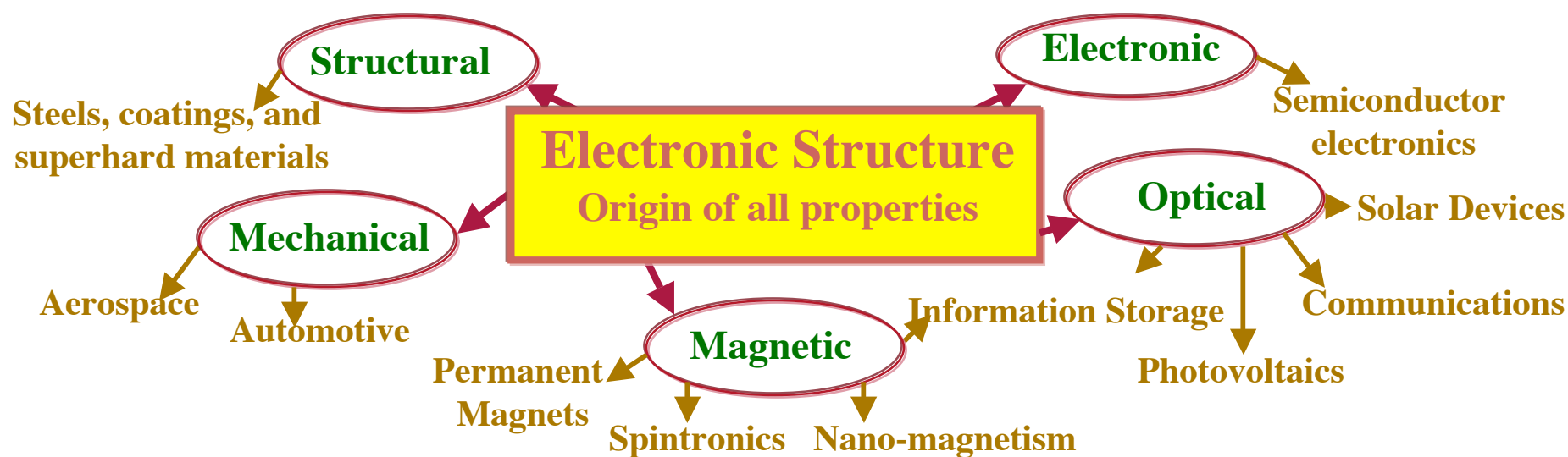
- Revolutionary development

- **Focus is on the charge density** – not on the many-electron wave function,  $\Psi$ , as in HF theory and all of chemistry
- But, what is the exchange-correlation potential,  $\mu_{xc}$ ?
- It is not known, but given the exact  $\mu_{xc}$  we would have the exact solution. To approximate  $\mu_{xc}$ , use the many-body solution for the **interacting** electron gas. The first term in the density expansion is  $\rho^{1/3}(r)$ .
- Local density approximation works because of the short range of the Fermi hole as shown by Slater (1951).



# Broad Impact of DFT-FLAPW in Electronic Structure and Properties

**Simulation /Modeling**  $\longrightarrow$  **Assisted materials design**



**FLAPW applications have produced a number of triumphs for DFT covering the whole range of properties.**

# Electronic Structure— Importance

- Basis for understanding fundamental properties of materials:
  1. elastic constants
  2. cohesive energies
  3. thermal properties
  4. magnetism (ordering and dynamics)
  5. optical response
  6. phase transitions
  7. surface phenomena
  8. interface phenomena
  9. transport

# Importance–*continued*

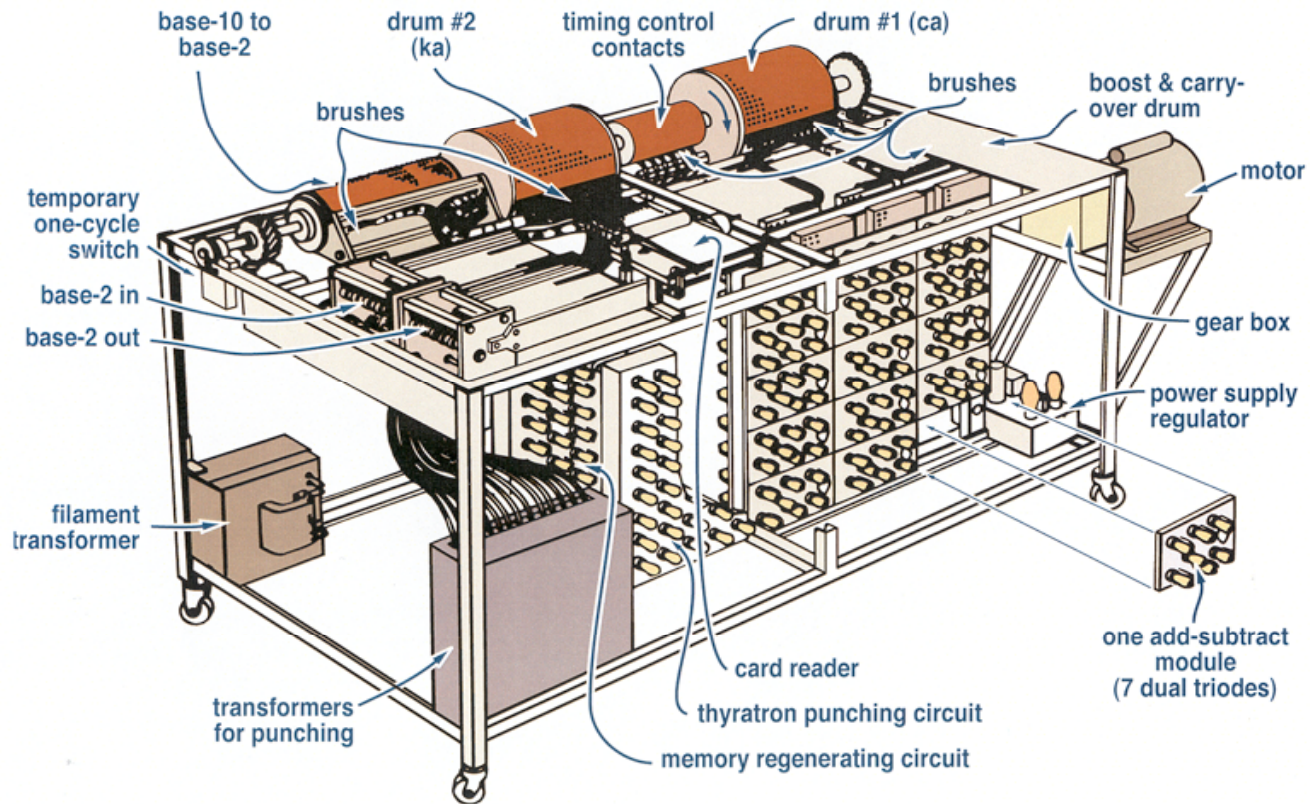
- Underpins the science for properties determined at mesoscale
  1. dislocations
  2. pinning (dislocations, magnetic domain walls, ...)
  3. grain boundaries
  4. cracks, defects, impurities, strains
  5. strength
  6. nucleation and growth of microstructures

# Importance–*continued*

- Coupled with modern computers, electronic structure “engineers” have teamed with experimental groups to
  1. design new magnetic materials for data storage
  2. design new microstructures for alloys applications
  3. investigate GMR interfaces
  4. study protein folding and biological issues
  5. etc.!

# History

## The Atanasoff-Berry Computer



# Density Functional Theory

1. Freeze the Lattice (separate nuclear coordinates)
2. Work only with electron Hamiltonian  
KE + electron-proton + electron-electron interactions
3. Original References:  
P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964)  
W. Kohn and L. Sham, *Phys. Rev.* **140**, A1133 (1965)  
*Phys. Rev.* **145**, 561 (1966).
4. All ground state properties of a many electron system are determined by a functional depending only on the density function. Variational principle for ground state energy.

# Density . . .*continued*

5. Some relevant equations:

$$E[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[\rho] \quad ,$$

Write the ele  $G[\rho] = T[\rho] + E_{\text{xc}}[\rho]$  .

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad ,$$

$$\left[ -\nabla^2 - \sum_I \frac{2Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \int 2 \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(\mathbf{r}) \right] \varphi_i = \varepsilon_i \varphi_i$$

Local Density Approximation (LDA)

$$E_{\text{xc}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}(\rho) d\mathbf{r} \ .$$

for spin polarized case

$$E_{\text{xc}}[\rho^+, \rho^-] = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}(\rho^+(\mathbf{r}), \rho^-(\mathbf{r})) d\mathbf{r} \ .$$

The exchange-correlation functional is obtained by many body calculations for the uniform interacting electron gas!



# Breakdown of LDA

1. Single atoms and surfaces (low density tails)
2. Self-interaction (e.g., hydrogen atom exchange)
3. Strongly correlated electron systems  
(e.g., rare earth materials,  $\text{La}_2\text{CuO}_4$ ,  $\text{Fe}_3\text{O}_4$ , etc.)

# Success of LDA

Nobel Prize: Walter Kohn, 1998 (in Chemistry!)

<http://www.physics.ucsb.edu/~kohn>

Nobel lecture: *Rev. Mod. Phys.* **71**, 1253 (1999).

## General References:

1. “The density functional formalism, its applications and prospects,”  
R. Jones, and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689-746 (1989).
2. For Chemistry perspective see “Advanced Electronic Structure  
Theory” by Dr. Fred Manby, <http://www.chm.bris.ac.uk/pt/manby/>
3. For MO - New Book by Antonov, Harmon, and Yaresko

# Beyond LDA

## 1. Weighted Density

O. Gunnarsson and R. Jones, *Physica Scripta*, **21**, 391 (1980).

## 2. Gradient Correction

J. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986).

A. Becke, *Phys. Rev. A* **33**, 2786 (1988).

## 3. Self Interaction Correction (SIC)

A. Svane and O. Gunnarsson, *Phys. Rev. Lett.* **65**, 1148 (1990).

Z. Szotek, W. Temmerman and H. Winter, *Phys. Rev. B* **47**, 4027 (1993); and for  $\text{La}_2\text{CuO}_4$ , A. Svane, *Phys. Rev. Lett.* **68**, 1900 (1992).

# Beyond . . .

## 1. LDA + U (treatment of strong correlation, 3d's, 4f's)

V. Anisimov, J. Zaanen, and O. Andersen, *Phys. Rev. B***44**, 943 (1991); V. Anisimov, I. Solov'ev, M. Korotin, M. Czyzyk, and G. Swatsky, *Phys. Rev. B***48**, 16929 (1993).

## 2. Orbital Polarization (account for Hund's second rule)

O. Eriksson, B. Johansson, R. Albers, A. Boring, and M. Brooks, *Phys. Rev. B***42**, 2707 (1990). O. Eriksson, M. Brooks, and B. Johansson, *Phys. Rev. B***41**, 7311 (1990).

## 3. Excitations (quasi-particles, Greens function approach)

### GW-approximation for the self-energy

L. Hedin and S. Lundqvist, *Solid State Physics*, **23** (1966)

L. Hedin, *Phys. Rev.* **139**, A796 (1965)

M. Hybertsen and S. Louie, *Phys. Rev. B***34**, 5390 (1986)

F. Aryasetiawan and O. Gunnarsson, *Phys. Rev. Lett.* **74**, 3221 (1995)

# Beyond . . .

## 7. Dynamical Mean Field Theory

### Frequency dependence of the self-energy

W. Metzner and D. Vollhardt, *Phys. Rev. Lett.* **62**, 324 (1995)

T. Pruschke, M. Jarell, and J. Freericks, *Adv. Phys.* **44**, 187 (1995)

A. Georges, G. Kotliar, W. Krauth, and M. Rozenberg. *Rev. Mod. Phys.* **68**, 13 (1996).

S. Savrasov, G. Kotliar, E. Abrahams, *Nature* **410**, 793 (2001)

S. Savrasov and G. Kotliar, preprint cond-mat/0106308 (2001)

A. Lichtenstein and M. Katsnelson, *Phys. Rev.* **B57**, 6884 (1998)

M. Katsnelson and A. Lichtenstein, *Phys. Rev.* **B61**, 8906 (2000)

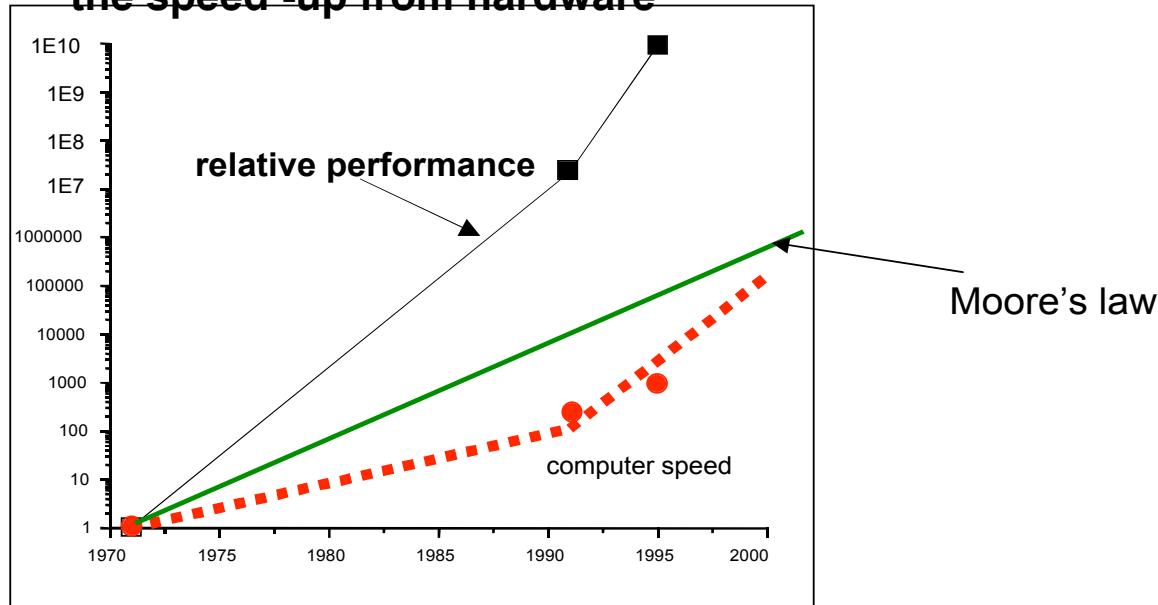
# Computational Materials Science—Future

## Some Past Predictions:

- 1943  
"I think there is a world market for maybe five computers."  
-- Thomas Watson, chairman of IBM
- 1949  
"Computers in the future may weigh no more than 1.5 tons."  
– *Popular Mechanics*, forecasting the relentless march of science
- 1977  
"There is no reason anyone would want a computer in their home."  
-- Ken Olson, president, chairman and founder of Digital Equipment Corp.
- 1981  
"640K ought to be enough for anybody"  
– Bill Gates

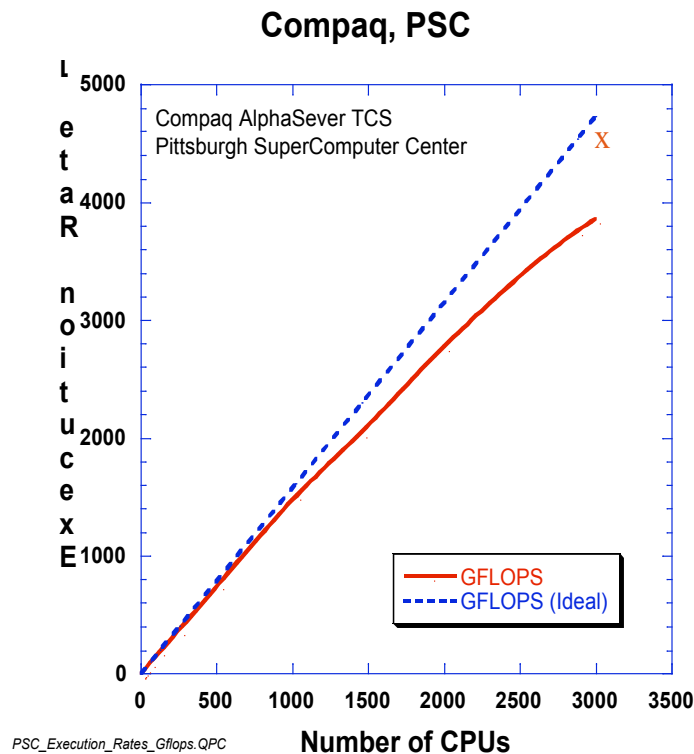
# Dramatic Advances in Theory and Algorithms

In Computational Materials Science the amplification from intellect (**new theory, algorithms, and insights**) is at least equal to the speed -up from hardware



*Relative performance increase of Ising model simulations compared the normalized speed of the computers the simulations were executed on. The dashed line is a schematic of the increase in peak performance of the fastest supercomputers since 1972.*

## Many CMS application codes scale on parallel computers



**4.58 Tflops!**

- **Similar data for other codes**
  - Paratec
  - FLAPW
- **Gordon Bell Prizes**
  - 1992 – KKR-CPA: Price Performance
  - 1995 - TBMD: Fastest real application
  - 1999 – LSMS: Fastest real application
- **$10^4$  improvement since 1988**
  - GB Prize
    - 1988 - 1 Gflop/s
    - 2001 - 11 Tflop/s